PATENT ABSTRACTS OF JAPAN

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(54) NORMAL TEMPERATURE-MELTING SALT AND ELECTROCHEMICAL DEVICE USING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a normal temperature-melting salt, not corroding, maintaining stability in a melted state at a normal temperature, useful for an electrolyte for an electrochemical device and a medium for electroplating, by mixing an aliphatic ammonium hydrogen maleate with a lithium salt.
SOLUTION: This normal temperature-melting salt having characteristics of an electrolyte high in ionic conductivity especially in a low-temperature range is obtained by mixing 1mol of an aliphatic ammonium hydrogen maleate comprising a conjugated anion of maleic acid, an aliphatic quaternary ammonium cation (e.g. methyltriethylammonium) with 0.1-10mol of a lithium salt [e.g. lithium bis(trifluoromethylsulfonyl) imidate. The normal temperature-melting salt is useful, for example, for an electrolyte for driving an electrolytic capacitor, is reacted with a defective part occurred during the use of an anode foil to form an oxidative coated film and to repair the part.

LEGAL STATUS

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DETAILED DESCRIPTION

[Detailed description]
[0001]
[The technical field to which invention belongs] this invention relates to the ordinary temperature fused salt which can be used as the electrolyte of electrochemical devices, such as a lithium primary cell, a lithium secondary battery, an electrolytic capacitor, an electric double layer capacitor, and an electrochromic display device, electrolysis synthesis, the medium for electroplating, etc.
[0002]
[Prior art] the solvents (for example, a gamma butyrolactone, N.N-dimethylformamide, propylene carbonate, a tetrahydrofuran, etc.) which are liquids from the former as an electrolyte of electrochemical devices, such as a lithium primary cell, a lithium secondary battery, an electrolytic capacitor, an electric double layer capacitor, and an electrochromic display device, -- Io -- the electrolytic solution which melted ionicity compounds (for example, a lithium perchlorate, a hoe fluoride tetraethylammonium, phthalic-acid tetramethylammonium, etc.) as a no-gene is used However, a solvent tends to volatilize and the electrolytic solution has the fault that a prolonged reliability is missing.
[0003] Then, the application of the ordinary temperature fused salt which does not use a solvent is proposed as an electrolyte (for example, Koura et al., J.Electrochem.Soc., 140 volumes, 602 pages, 1993). As ordinary temperature fused salt, the complex (Takahashi, electrochemistry, 59 volumes, 14 pages, 1991) of the halogenide of the fourth class ammonium of aromatic series, such as N-butyl pyridinium and N-ethyl-N'-methyl imidazolium, and an aluminum halide, the mixture (C. A.Angell et al., Nature, 362 volumes, 137 pages, 1993) of two or more sorts of lithium salt, etc. are known. However, the former complex has a problem in corrosive [by halogenide ion], and the latter is an unstable supercooled liquid thermodynamically and has the trouble of solidifying with time.
[0004]
[Object of the Invention] It is going to offer the ordinary temperature fused salt which this invention does not have corrosive, and keeps stable the status that melting was carried out in ordinary temperature (25 degrees C), and has a large temperature requirement, and has the property of the electrolyte with an ion conductive ceramics especially high also in a low-temperature region.
[0005]
[The means for solving a technical problem] this invention offers the electrochemical device using maleic-acid hydrogen aliphatic quarternary ammonium salt, the ordinary temperature fused salt which comes to mix lithium salt, and it.
[0006]
[Gestalt of implementation of invention] The maleic-acid hydrogen aliphatic quarternary ammonium salt used for this invention consists of the conjugate anion and the fourth class ammonium cation of aliphatic series of a maleic acid. As the fourth class ammonium cation of aliphatic series, the number of total carbons of four alkyl groups can illustrate the tetrapod alkylammonium of 4-16, for example, tetramethylammonium, a tetraethylammonium, tetrabuthyl ammonium, methyl triethyl ammonium, methyl tributyl ammonium, ****** trimethylammonium, etc. Unsymmetrical tetrapod alkylammonium, such as methyl triethyl ammonium, methyl tributyl ammonium, and ****** trimethylammonium, is desirable of these.
[0007] If the example of the maleic-acid hydrogen aliphatic quarternary ammonium salt used for this invention is given, a maleic-acid hydrogen methyl triethyl ammonium salt, a maleic-acid hydrogen tetraethylammonium salt, a maleic-acid hydrogen ****** trimethylammonium salt, etc. will be mentioned. These maleic-acids hydrogen aliphatic quarternary ammonium salt is usually used independently.
[0008] As lithium salt used for this invention, the lithium salt (lithium salt [of] and inorganic acids, such as lithium triphloromethanesulfonate a p-toluenesulfonic-acid lithium, a screw (********** methyl sulfo nil) imido-acid lithium, and a tris (** ******* methyl sulfo nil) carbon acid lithium] [, [LiNO3, LiSCN, LiClO3, LiClO4, LiBF4, LiPF6, LiAsF6, LiSbF6], etc.) of an organic acid can be illustrated. [for example,] A screw (**** * *** methyl sulfo nil) imido-acid lithium, a lithium perchlorate, a tetrapod

fluoroboric-acid lithium, a hexafluoro phosphoric-acid lithium, and a tris (********** methyl sulfo nil) carbon acid lithium are desirable of these, and its lithium salt of organic acids, such as a screw (********** methyl sulfo nil) imido-acid lithium, is especially desirable.

[0009] Although the ordinary temperature fused salt of this invention is obtained by mixing the maleic-acid hydrogen aliphatic quarternary ammonium salt more than the above-mentioned kind, and the lithium salt more than a kind with a suitable mixing ratio, the mixing ratio is a mixing ratio which is not solidified even if it is decided according to the modality of salt to mix and it cools to a room temperature after lysis. Generally, lithium salt is used at a rate of 0.1-10 mols to one mol of maleic-acid hydrogen aliphatic quarternary ammonium salt. Since it serves as a liquid stable also in a low-temperature region at the same time it keeps stable the status that did not volatilize outside in the elevated temperature and melting was carried out in ordinary temperature, since the ordinary temperature fused salt of this invention does not contain the solvent, it can be used as the electrolyte excellent in the temperature characteristic which bears the prolonged reliability of electrochemical devices, such as a lithium primary cell, a lithium secondary battery, an electrolytic capacitor, an electric double layer capacitor, and an electrochromic display device, and a medium for electrolysis synthesis or electroplating. The electrochemical device using especially the ordinary temperature fused salt of this invention as an electrolyte is expected very much as what solves the trouble of the electrolyte (electrolytic solution) of the conventional liquid. For example, when it supposes that it is as an electrolyte for an electrolytic capacitor drive and it uses it, in the element which formed the dielectric oxide film in the front face of valve action metals, such as an aluminum foil, by the anodizing, considered as the anode plate foil, and separators, such as electrolysis paper, were made to intervene between the cathode foils which counter this, and made these the laminating or the **** type, the thing which makes the ordinary temperature fused salt of this invention intervene between this anode plate foil and a cathode foil is mentioned. In the case of such intended use, it acts on a part for the defective part which it was desirable to have had electrical conductivity also in the state of any of a solid-state and a liquid as for especially this ordinary temperature fused salt, and was produced in the anode plate foil-like use middle class, and has the property to form and compensate an oxide film.

[0010]

[Example] Although an example is given to below and this invention is explained to it still concretely, this invention is not limited at all by these examples.

(Example 1) In the glove box under the nitrogen ambient atmosphere, maleic-acid hydrogen methyl triethyl ammonium (MTEAM) and the screw (********** methyl sulfo nil) imido-acid lithium (LiTFSI) were mixed by the mole ratio 9:1, heating melting was carried out to about 80 degrees C, and the ordinary temperature fused salt which is a uniform liquid after **** was obtained. Using the cell for closed mold conductivity measurement, the impedance analyzer, and the thermostat, this ordinary temperature fused salt was inserted into the stainless steel inter-electrode ground well through the Teflon nature spacer with a diameter [of 1cm], and a thickness of 1mm, the impedance of a cell was measured at 5Hz - 13MHz of frequency ranges, and temperature-requirement 100--25 degree C, ionic conductivity was measured in oscillation level 500mV, and it was shown in drawing 1 . The ionic conductivity in 30 degrees C was 1.4x10 to 3 S/cm. After 150 day progress did not change but the ionic conductivity of this thing was 1.4x10 to 3 S/cm.

[0011] (Example 2) In the example 1, the ionic conductivity when obtaining ordinary temperature fused salt similarly was shown in drawing 1 except having changed the mixed mole ratio of MTEAM and LiTFSI into 8:2. In addition, the ionic conductivity in 30 degrees C was 9.8x10 to 4 S/cm. Moreover, most ionic conductivity after 150 day progress was not falling.

[0012] (Example 1 of a comparison) In the glove box under the nitrogen ambient atmosphere, a methyl-benzoate triethyl ammonium salt (MTEAB), an acetic-acid lithium (LiOAc), and LiTFSI were mixed by the mole ratio 7:2:1, heating melting was carried out to about 150 degrees C, and the uniform liquid was obtained. This was quenched using the stainless steel plate cooled beforehand, and ordinary temperature fused salt was obtained. Except having made measurement of the ionic conductivity of this ordinary temperature fused salt into temperature-requirement 80--10 degree C, it carried out on an example 1 and these conditions, and was shown in drawing 1 . In addition, the ionic conductivity in 30 degrees C was 1.1x10 to 4 S/cm. The ionic conductivity after 60 day progress of this thing was 1.0x10 to 4 S/cm.

[0013] (Example 2 of a comparison) In the example 1 of a comparison, except having changed the mixed mole ratio of MTEAB, LiOAc, and LiTFSI into 8:1:1, ordinary temperature fused salt was obtained similarly and the ionic conductivity was shown in drawing 1 . In addition, the ionic conductivity in 30 degrees C was 0.7x10 to 4 S/cm. Moreover, as for the ionic conductivity after 60 day progress, the left was not falling.

[0014]

[Effect of the invention] The ordinary temperature fused salt which this invention does not have corrosive, and keeps stable the status that melting was carried out in ordinary temperature, and has a large temperature

* NOTICES *

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CLAIMS

[Claim]
[Claim 1] Maleic-acid hydrogen aliphatic quarternary ammonium salt and ordinary temperature fused salt which comes to mix lithium salt.
[Claim 2] Ordinary temperature fused salt given in the claim 1 whose numbers of total carbons of the substituent of the ammonium of maleic-acid hydrogen aliphatic quarternary ammonium salt are 4-16.
[Claim 3] The claim 1 whose lithium salt is at least one sort chosen out of a screw (********** methyl sulfo nil) imido-acid lithium, the lithium perchlorate, the tetrapod fluoroboric-acid lithium, the hexafluoro phosphoric-acid lithium, and the tris (********** methyl sulfo nil) carbon acid lithium, or ordinary temperature fused salt given in 2.
[Claim 4] The claim 1 characterized by the ratio of maleic-acid hydrogen aliphatic quarternary ammonium salt and lithium salt being 1:0.1-10 (mole ratio), or ordinary temperature fused salt given in either of 3.
[Claim 5] The electrochemical device characterized by using as an electrolyte the ordinary temperature fused salt which comes to mix maleic-acid hydrogen aliphatic quarternary ammonium salt and lithium salt.

[Translation done.]

requirement, and has the property of the electrolyte with an ion conductive ceramics especially high also in a low-temperature region can be offered. The electrochemical devices which used this ordinary temperature fused salt, such as an electrolytic capacitor and a lithium secondary battery, can solve the trouble in the point of long-term reliabilities, such as volatilization of the solvent at the time of using the electrolytic solution conventionally, and the corrosive trouble at the time of using the ordinary temperature fused salt known conventionally.
[0015]

[Translation done.]

TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to the ordinary temperature fused salt which can be used as the electrolyte of electrochemical devices, such as a lithium primary cell, a lithium secondary battery, an electrolytic capacitor, an electric double layer capacitor, and an electrochromic display device, electrolysis synthesis, the medium for electroplating, etc.

PRIOR ART

[Prior art] the solvents (for example, a gamma butyrolactone, N.N-dimethylformamide, propylene carbonate, a tetrahydrofuran, etc.) which are liquids from the former as an electrolyte of electrochemical devices, such as a lithium primary cell, a lithium secondary battery, an electrolytic capacitor, an electric double layer capacitor, and an electrochromic display device, -- Io -- the electrolytic solution which melted ionicity compounds (for example, a lithium perchlorate, a hoe fluoride tetraethylammonium, phthalic-acid tetramethylammonium, etc.) as a no-gene is used However, a solvent tends to volatilize and the electrolytic solution has the fault that a prolonged reliability is missing.

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EFFECT OF THE INVENTION

[Effect of the invention] The ordinary temperature fused salt which this invention does not have corrosive, and keeps stable the status that melting was carried out in ordinary temperature, and has a large temperature requirement, and has the property of the electrolyte with an ion conductive ceramics especially high also in a low-temperature region can be offered. The electrochemical devices which used this ordinary temperature fused salt, such as an electrolytic capacitor and a lithium secondary battery, can solve the trouble in the point of long-term reliabilities, such as volatilization of the solvent at the time of using the electrolytic solution conventionally, and the corrosive trouble at the time of using the ordinary temperature fused salt known conventionally.

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TECHNICAL PROBLEM

[Object of the Invention] It is going to offer the ordinary temperature fused salt which this invention does not have corrosive, and keeps stable the status that melting was carried out in ordinary temperature (25 degrees C), and has a large temperature requirement, and has the property of the electrolyte with an ion conductive ceramics especially high also in a low-temperature region.

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MEANS

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[0006]

[Gestalt of implementation of invention] The maleic-acid hydrogen aliphatic quarternary ammonium salt used for this invention consists of the conjugate anion and the fourth class ammonium cation of aliphatic series of a maleic acid. As the fourth class ammonium cation of aliphatic series, the number of total carbons of four alkyl groups can illustrate the tetrapod alkylammonium of 4-16, for example, tetramethylammonium, a tetraethylammonium, tetrabuthyl ammonium, methyl triethyl ammonium, methyl tributyl ammonium, ****** trimethylammonium, etc. Unsymmetrical tetrapod alkylammonium, such as methyl triethyl ammonium, methyl tributyl ammonium, and ****** trimethylammonium, is desirable of these.

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[Translation done.]

DESCRIPTION OF DRAWINGS

[An easy explanation of a drawing]
[Drawing 1] It is drawing showing a correlation of the temperature and the ionic conductivity of ordinary temperature fused salt.

[Translation done.]

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DRAWINGS

[Drawing 1]

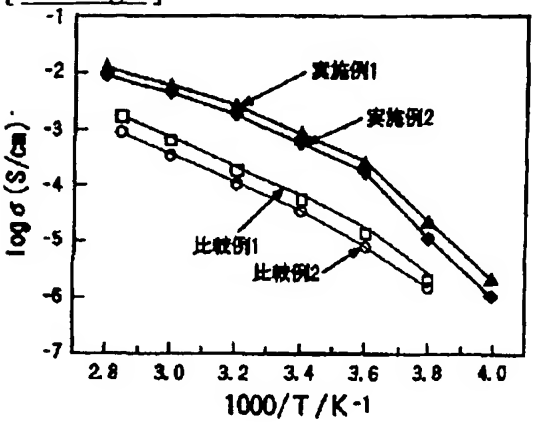

図1. 常温溶融塩のイオン導電率

[Translation done.]